

ACIDIC PRECIPITATION IN ONTARIO STUDY

AN EVALUATION OF SAMPLER TYPES AND SAMPLING PERIODS FOR MEASUREMENTS OF WET AND DRY DEPOSITION

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Dr. David Balsillie, Director
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ACIDIC PRECIPITATION IN ONTARIO STUDY**AN EVALUATION OF SAMPLER TYPES AND SAMPLING PERIODS
FOR MEASUREMENTS OF WET AND DRY DEPOSITION**

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CONCLUSIONS

In this study, the intra-sampler measurement precision, the equivalency of different types of samplers, the equivalency of sampling periods, the collection efficiency for samplers used in the APIOS network, the evaporation and dry contamination effects associated with daily and cumulative sampling and the difference in deposition determined from daily and cumulative sampling protocols have been examined.

Major conclusions are:

1. Reproducibility of daily measurements of acid/base-related parameter concentrations by Aerochem Metrics samplers is better than 93%, and is somewhat poorer for other major ions (Section 4.1.1.1).
2. Sampling reproducibility of precipitation concentrations of acid-base related parameters over a 28 d interval with Sangamo (M.I.C. Type A) samplers is better than 88%; for trace metals and other major ions it is poorer (Section 4.1.1.2).
3. Accuracy was investigated in terms of evaporative losses and dry deposition being a source of error in daily precipitation sampling (Section 4.3.2). Errors due to these factors were found to be small with wet-only Aerochem Metrics samplers. Even though there is some indication of entry of dry contamination to some samples, on average, the contamination on a daily basis is negligible and is within the laboratory precision. Similarly, on average, evaporative losses over a daily basis are minimal. However, some of the sampler equivalency tests suggested that the Aerochem Metrics sampler may have a small source of error due to relatively sluggish sensor response (which results in systematic missing of the initial portion of events), which is difficult to quantify, but leads to inter-sampler differences (when compared to Sangamo and SES bulk samplers) of less than about 15% for the acid-base related parameters (Section 4.2).
4. Over a typical cumulative sampling period (28d or 1 month) under field conditions most acid/base parameters show little change (Section 4.3.1.2). K^+ and Cl^- concentrations are increased, possibly due to sorption from the

polyethylene/nylon bags. However, the changes are usually small compared to the concentrations typically observed in the network samples. Ammonium is found to be environmentally unstable and can fluctuate up or down in concentration.

5. The effect of the major sources of errors in sampling, viz. evaporative losses and dry deposition, on accuracy of precipitation chemistry measurements over a 28d period has been assessed. On average, less than 10% evaporative losses were found (Sections 4.3.1.3 and 4.4.1.3). Dry deposition is observable for the soil-related parameters, and, on average, could be as high as 11% for Ca^{++} and 31% for Mg^{++} . There is little effect on H_t^+ , H_f^+ , $\text{SO}_4^{=}$, NO_3^- and Na^+ due to dry deposition (Section 4.3.1.4). On the basis of these results, we estimate that the overall accuracy of an annual average concentration or a deposition (i.e., concentration multiplied by precipitation gauge depth) value, based on a 28 d collection period, for the acid/base-related parameters is about 10%. For the other ions, the accuracy is poorer.
6. Reproducibility of 24-hour air concentration measurements (with filter packs coupled to a sequential sampler, Metrex SAS 8-25) for the acid-base related parameters is better than 90% (Section 4.1.2).
7. Reproducibility of air concentration measurements of $\text{SO}_4^{=}$, NO_3^- and HNO_3 on a 28 d basis with filter packs and a lo-vol Metrex AS-2 sampler is better than 93%. That of SO_2 is poorer, about 85% (Section 4.1.2).
8. Concentration differences between the wet-only Sangamo and Aerochem Metrics samplers for acid-base related parameters sampling on a daily basis are less than 14% (Section 4.2). They are higher for the soil-related and road salt-related species, up to 40% in some cases. The Sangamo concentrations are higher than those of Aerochem Metrics samplers, reflecting the fact that the Sangamo sensor is more sensitive than that of Aerochem Metrics. However, the collection efficiency of the Aerochem Metrics sampler is somewhat higher than that of Sangamo (which has a smaller collection area), resulting in comparable loading observations with the two samplers (loading is defined as concentration multiplied by the depth of sample in the precipitation chemistry sampler).

9. The median absolute difference between the 28 d cumulative sampler concentrations and the accumulated daily concentrations is less than 12% for the acid-base related parameters and is higher for the soil-related parameters (Section 4.4.1). Calculated deposition based on cumulative and accumulated daily measurements could differ by 12% for acid-related species and more for other parameters. Not all the 12% is due to the difference in sampling periods. Part of it is due to the differences in sampler type (i.e., Sangamo v.s. Aerochem Metrics) and missing chemical analyses in the daily samples because of insufficient sample volume.
10. Air concentrations of SO_2 and $\text{SO}_4^{=}$ sampled over a 28 d interval with low volume samplers are comparable to those obtained from daily samplers over the same period (Section 4.4.2). The corresponding total NO_3^- concentration is higher for the 28 d sample as a result of the sampling method used. However, it amounts to only 3% in terms of the median percentage absolute difference.

1. INTRODUCTION

Under the auspices of the Acidic Precipitation in Ontario Study (APIOS) of the Ontario Ministry of the Environment, the Air Resources Branch operates two wet and dry deposition networks on a daily and on a cumulative (monthly or 28 day) basis. The wet deposition measurements were first started in 1980 and the networks were fully implemented in early 1981. The dry deposition network was not fully implemented until late 1981. In the daily precipitation monitoring network, Aerochem Metrics wet-only and SES bulk samplers were initially used in the May to October period and November to April period respectively. From May, 1982 onward, Aerochem Metrics samplers were used year round. In the cumulative network Sangamo (M.I.C. Type A) wet-only samplers have been used since the inception of the network. In the dry deposition case, since there is no routine method for direct dry deposition measurement, it is inferred from the pollutant air concentration and its deposition velocity. Air concentration is determined with a low volume filter pack sampling method using Metrex samplers. Details of the equipment and protocols used in the network are given elsewhere (Chan et al., 1982 and 1985). This report deals with an assessment of the precision, bias, and accuracy of the various measurements made in the APIOS deposition monitoring program.

Several factors could bring about errors in deposition measurements.

1. Siting:

This could be a large source of error if the site is poorly chosen or non-representative for other reasons with respect to the objectives of the sampling program.

2. Sampling:

- a. Errors are due to poor sample representativeness as a result of the sampling instrumentation used.
- b. Errors may arise due to sample degradation in the field.
- c. Container wall absorption/desorption may also introduce errors.
- d. Evaporation and contamination by dry deposition under field conditions are also potential sources of error.

3. Sample Handling and Laboratory Analysis:

Sample handling in the field and laboratory, potential sample deterioration and chemical analyses can all introduce errors into the measurement results.

In this study, it is assumed that the sites used are well chosen and the emphasis is to understand sources of error associated with sampling in the field. Errors arising from poor site location, sample handling and chemical analysis will not be separately addressed here.

The objectives of this report are fourfold:

1. To determine measurement precision of different sampler types, e.g. Aerochem Metrics, Sangamo (M.I.C. Type A) and SES bulk precipitation samplers, and filter packs in conjunction with Metrex Lo-Vol air samplers.
2. To assess the comparability of different sampler types, e.g. Aerochem Metrics vs. Sangamo samplers, Aerochem Metrics vs. SES bulk samplers, and Sangamo vs. SES bulk samplers.
3. To evaluate the equivalency of different air and precipitation sampling intervals, e.g. daily vs. monthly (or four-weekly), and to determine the reason for any differences.
4. To estimate the accuracy of daily and cumulative wet deposition measurements, and the magnitude of the major suspected sources of error.

2. EXPERIMENTAL

2.1 Sampling Precision and Sampler Equivalency

Duplicate sampling with two samplers of the same type co-located at several sites has been carried out at Dorset ($45^{\circ}13'23''\text{N}$, $78^{\circ}55'49''\text{W}$); Longwoods ($42^{\circ}53'02''\text{N}$, $81^{\circ}28'50''\text{W}$); Railton ($44^{\circ}22'34''\text{N}$, $76^{\circ}35'33''\text{W}$) and Charleston Lake ($44^{\circ}29'54''\text{N}$, $76^{\circ}02'30''$). The co-located sampling results available from late 1980 to the end of 1983 at three APIOS sampling stations will be used to evaluate the precision of measurements and equivalency of different sampler types, i.e. Aerochem Metrics, SES bulk, Sangamo samplers, and air filter packs in conjunction with Metrex samplers. The assessments are carried out for both daily and 28-day protocols.

2.2 Sampling Accuracy of Precipitation Measurements

There is no simple way to assess the accuracy of precipitation chemistry measurements. Hence the following approximate approach was used. Standard solutions or composites of precipitation samples of known chemical concentration were subjected to the chain of routine sampling steps. A known volume of the solution was introduced into the sampling container at the beginning of a sampling period extending to either 24 hours or 28 days. The control samplers were shielded in shelters from the collection of precipitation, however, their sensors were extended and exposed to the atmosphere in such a way that they (i.e. the sensors) would come into contact with precipitation. Thus, during precipitation periods, the hood of the sampler would be uncovered, however the samplers would not collect precipitation samples since they were shielded. Regular sample handling and analytical procedures were used. A comparison was made of the initial and final sample volumes and concentrations under different laboratory and field conditions (see Section 4.3.1) to determine whether any changes were introduced in the course of the sampling scheme (such as contamination during sample handling, chemical deterioration, evaporation losses in the field, or contributions from dry deposition either while the collection vessel lids are off during precipitation, or by any air "leakage" into the covered vessels during dry periods). Figure 1 shows the experimental setup.

A number of related experiments were also carried out as part of this particular study. For example, evaporative effects were examined independently by storing a known volume of water in several samplers under field conditions, with the cover closed (and the sampler turned off), and comparing the initial and final volumes (this approach assumes that the evaporative loss during precipitating periods, when the cover would be normally off - roughly 10% of the time - is comparable to that with the cover on). Chemical changes in the sampler (apart from those introduced by dry deposition) were examined by storing precipitation in a sealed bag, which was left in the field, in a sampler bucket, over the collection period, and then comparing the initial and final concentration for a number of constituents.

Note that this approach assumes that a standard solution, or composite precipitation sample, will behave in a manner similar to a real-world, freshly-collected sample. This is probably true for most of the precipitation constituents of interest, but may not be for hydrogen ions and the nitrogen compounds, which have shown rapid changes in some samples (Atkins, 1975; Peden and Skowron, 1978). In this sense, the composite samples used here (which may have been chemically "stabilized" compared to freshly -collected samples) may not adequately simulate reality, at least for hydrogen ions and the nitrogen compounds.

Experiments of this type for the cumulative sampling scheme were carried out at Dorset over the period April 27, 1982 to August 17, 1982 and April 26, 1983 to November 6, 1984, thus including samples from all the seasons of the year. The daily sampling experiments were conducted over the period October 7, 1982 to November 11, 1982 and June 12, 1984 to September 6, 1984.

2.3 Sampling Protocol Equivalency

Simultaneous sampling with an Aerochem Metrics sampler, operating on a daily basis and a Sangamo sampler on a cumulative (monthly or 28 day), basis was carried out at Dorset and Fernberg from 1980-1983. The result of the daily measurements accumulated over a monthly or 28 day period is compared to that of a single cumulative measurement made over the same period to evaluate their equivalency. This assessment was carried out for both air and precipitation samplers.

3. ANALYSIS APPROACH

This section describes the mathematical formulation used in the assessment of sampling precision, sampling accuracy and sampling period equivalency.

3.1 Sampling Precision

There is no conventionally accepted definition of sampling precision. In his assessment of precipitation concentration data, Topol et al. (1982) expressed sampling precision in terms of the ratio of the median absolute difference between duplicate samples and the median concentration. In our analysis, we have taken a somewhat different approach which we believe to have a clearer physical meaning. Instead of calculating the ratio of the median difference and mean concentration values, we determine the median of the ratios. There are various ways to express the normalized concentration difference and their inter-relationships are shown below.

- (i) Measurement precision is a measure of how reproducible the measurements are. The more precise (or reproducible) the measurements are, the smaller the quantity X is.

$$X = \frac{|C_1 - C_2|}{C_1} \text{ or } \frac{|C_2 - C_1|}{C_2} \quad (1)$$

- (ii) Measurement precision is expressed as the ratio of the absolute difference to the mean:

$$Y = \frac{|C_1 - C_2|}{(C_1 + C_2)/2} = \frac{2 |C_1 - C_2|}{C_1 + C_2} \quad (2)$$

- (iii) Coefficient of variation (C.O.V.)

$$\begin{aligned} Z = \text{C.O.V.} &= \frac{\text{std. dev.}}{\text{mean}} = \frac{(C_1 - (C_1 + C_2)/2)^2 + (C_2 - (C_1 + C_2)/2)^2}{(C_1 + C_2)/2} \\ &= \frac{\sqrt{2} |C_1 - C_2|}{C_1 + C_2} \quad \text{for } n = 2 \end{aligned} \quad (3)$$

As seen, these three entities are inter-related, namely:

$$Y = \sqrt{2} \ Z \simeq X \text{ (if } C_1 \ C_2) \quad n=2$$

In our calculations, X is reported for sampler precision and as C_1 and C_2 are usually very similar, the results are about the same as Y.

Hoehne (1971) has expressed duplicate sampling results in terms of bias and precision, and his approach was also used here.

$$\text{bias} = (1/n) \sum_{i=1}^n (C_{1i} - C_{2i}) \quad (4)$$

$$\text{functional precision} = \pm \sqrt{(1/n) \sum_{i=1}^n (C_{1i} - C_{2i})^2} \quad (5)$$

and

$$\text{precision} = (1/n) \sqrt{\sum_{i=1}^n (C_{1i} - C_{2i})^2 - \left[(1/n) \sum_{i=1}^n (C_{1i} - C_{2i}) \right]^2} \quad (6)$$

The above entities give results in terms of their absolute magnitudes and are site specific (in the sense that the long-term absolute value of the concentration varies from site to site). Essentially, precision is the standard deviation of the measurement bias. If these values are normalized to their mean measurements, they yield information relative to the measurement values and hence, may be non-site specific. In this study, the normalized bias and normalized precision are also included so that the results may be applied to other sites.

The normalized quantities are obtained by replacing C_{2i}

by $(C_{1i} + C_{2i})/2$, for example

$$\text{normalized bias} = (1/n) \sum_{i=1}^n \left[\frac{C_{1i} - ((C_{1i} + C_{2i})/2)}{((C_{1i} + C_{2i})/2)} \right] \quad (7)$$

and

$$\begin{aligned} &\text{normalized functional precision} \\ &= \sqrt{(1/n) \sum_{i=1}^n (C_{1i} - (C_{1i} + C_{2i})/2)^2 - \left[(1/n) \sum_{i=1}^n (C_{1i} - (C_{1i} + C_{2i})/2) \right]^2} \end{aligned} \quad (8)$$

3.2 Sampling Accuracy

In the experiments described in Section 2.2, accuracy was estimated by comparing the initial concentrations of the standard solutions to their final concentrations, after subjecting them through the chain of steps encountered by a "real-world" precipitation sample.

Results are given in terms of the linear correlation coefficient, slope and intercept, based on the Bartlett linear regression method (Smith et al., 1983). The Bartlett regression method is judged to be more appropriate than linear least square regression when both variables (in this case initial and final concentration measurements) have uncertainties in them. The difference in results is also expressed in terms of normalized absolute difference and normalized bias.

3.3 Sampling Protocol Equivalency

Precipitation depth weighted concentrations of the daily samples over a monthly or 28 day sampling period, and the corresponding deposition, were calculated and compared with the single cumulative measurement of concentration and deposition over the same interval. The bias of the 28 day (Sangamo Samplers) vs. accumulated daily (Aerochem Samplers) measurements was compared to that using the same samplers but operating on a daily basis.

Equivalency is expressed in terms of the absolute difference of one measurement with respect to the mean of the two measurements by the two sampler types. As each individual measurement has certain errors, the mean value of the two is more representative of the true value.

$$\begin{aligned} W &= \frac{|C_1 - (C_1 + C_2)/2|}{(C_1 + C_2)/2} = \frac{|C_2 - (C_1 + C_2)/2|}{(C_1 + C_2)/2} \\ &= \frac{|C_1 - C_2|}{C_1 + C_2} \end{aligned} \tag{9}$$

Bartlett regression analysis was also performed to examine the relationship between daily and cumulative samples.

3.4 Evaluation of Collection Efficiency and Evaporative Effects

Collection efficiency and evaporative effects associated with 28-day sampling were determined in two different ways - (1) by considering only the precipitation volume data, and (2) by evaluating the long-term precipitation chemistry data collected by a co-located 28-d and daily sampler.

The first approach is somewhat more straightforward. Evaporative losses over a 28-d period can be obtained directly from the experiment described in Section 2.2 (covered sampler charged with a known volume of liquid and left in the field over a 28-d period, with volume changes over the period being attributed to evaporation). Once the average evaporative losses are known (over an annual or seasonal period), the collection efficiency can be isolated by comparing the sampler depth with a co-located standard gauge depth (assumed to have no evaporation losses, and a collection efficiency of 100%).

The second approach requires one to make the assumption that a daily sampler collects precipitation samples in a perfectly representative manner (i.e., even if the collection efficiency is not 100%, the resulting sample is still representative of the event), and is discussed below.

Let us define V_i , D_i and C_i to represent the volume (or equivalent depth), deposition and concentration of a precipitation sample. i is equal to 0, 1 and 2 for the true precipitation sample, an actual sample with no evaporative losses but less than perfect collection efficiency, and an actual sample with both less than 100% collection efficiency and evaporative losses respectively.

With no evaporative losses, the collected sample will have the following characteristics:

$$\begin{aligned}V_1 &= V_0 M \\D_1 &= D_0 M \\C_1 &= C_0 = D_1/V_1 = D_0/V_0\end{aligned}$$

where M is the collection efficiency.

If the collected sample suffers also from evaporative losses, then:

$$\begin{aligned}V_2 &= V_1 R = V_0 MR \\D_2 &= D_1 \\C_2 &= D_2/V_2 = D_0 M/V_0 MR = D_0/V_0 R\end{aligned}$$

where R is the ratio of sample volumes with and without evaporation.

Hypothetically, collection efficiency affects only the collected sample volume and hence deposition; it does not have any effect on the resulting concentration assuming that the collection efficiency is uniform for all types of precipitation. Similarly, evaporation should affect only the volume and hence concentration, but not the deposition. Volume, of course, is affected by both collection efficiency and evaporation.

If a primary standard representative of the original precipitation is available, it is feasible to establish the extent of effects due to both collection efficiency and evaporation. It is assumed here that the data from the daily sampling network can be used for this purpose, for the following reasons: evaporation is minimal with wet-only samples collected on a daily basis, and therefore the observed concentrations should correspond to those of the actual fallen precipitation. The imperfect collection efficiency can be taken care of by the use of results from a co-located standard rain gauge or Nipher-shielded snow gauge in the deposition calculations. We assume here that problems due to variations in precipitation concentration throughout the course of an event (as when the most concentrated portions of a precipitation event, which often occur at the beginning, are missed, due to a delay in sampler opening) are not significant (See Section 4.2). That is to say, we assume that C_o , D_o and V_o can be replaced by C_d , D_d and V_d where d indicates an accumulated daily value and V_d = accumulated daily primary gauge depth over the cumulative sampling period. To simplify our discussion, we represent C, V, D of the cumulative samples by C_c , V_c and D_c .

It is obvious that

$$\frac{V_2}{V_o} = \frac{V_c}{V_d} = \frac{V_o M_c R_c}{V_o} = M_c R_c \quad (10)$$

$$\frac{D_2}{D_o} = \frac{D_c}{D_d} = \frac{V_c C_c}{V_d C_d} = \frac{(\text{loading}*)_c}{(\text{deposition}*)_d} = \frac{D_o M_c}{D_o} = M_c \quad (11)$$

$$\frac{C_o}{C_2} = \frac{C_d}{C_c} = \frac{(D_o/V_o)}{(D_o/V_o R_c)} = R_c \quad (12)$$

and (11) x (12) = (10)

* Loading is defined as concentration multiplied by the depth of sample in the precipitation chemistry sampler. Deposition is concentration multiplied by precipitation gauge depth.

Here M_c and R_c are the parameters of interest, the approximate collection efficiency and retention efficiency after evaporation in the cumulative sampling scheme. The evaporative effect is equal to $(1-R_c)$. It should be borne in mind that larger uncertainties in the results would occur if the sample concentrations are at or near the detection limits.

Since M_c and R_c may vary from site to site and from season to season, therefore instead of correcting for individual results in the cumulative network because of imperfect collection efficiency and evaporation, a gross error assessment is attempted of the uncertainty associated with the reported deposition calculated both using measured concentration and precipitation gauge depth based on the grand average for individual parameters.

4. RESULTS AND DISCUSSION

4.1 Sampler Precision

4.1.1. Precipitation Samplers

4.1.1.1 Daily Sampling

Results of the evaluation of daily Aerochem Metrics and SES samplers used in the APIOS network are summarized in Tables 1 to 4.

Tables 1 and 2 are median absolute difference results using equation (1) in Section 3.1 for concentration and loading (sample concentration x sample depth). Deposition (sample concentration x gauge depth) results are identical to those of the concentration because the same gauge is used to determine precipitation depth in the calculation for both duplicate samplers. Conductivity results are not shown here as they reflect the collective difference of the various ionic species present in the precipitation samples and they give little useful information on their own. There are minor variations from site to site and from parameter to parameter. In both Aerochem Metrics and SES bulk samplers, the reproducibility (1 (one) minus normalized absolute difference) of concentration measurements based on all station data for the acid-base related parameters (e.g. H_f^+ , H_t^+ , $SO_4^{=}$, NO_3^- and NH_4^+) is better than 93%. Reproducibility for the soil-related (Ca^{++} , Mg^{++} and K^+) and road salt-related (Na^+ and Cl^-) parameters is poorer, reflecting the fact that some of these concentrations are at the detection limit, and showing the effects of possible local contamination. Reproducibility of sample depth (SDP) is very good, better than 97% for both sampler types. Reproducibility for loading measurements is quite good but is somewhat worse than that of the concentration measurements. In all cases, reproducibility of the SES bulk samplers is better than that of the Aerochem Metrics samplers and this is most-likely due to the larger opening area, and no mechanical problem in the former.

Tables 3 and 4 show the bias and precision results of precipitation concentrations based on equations (4) and (5) in Section 3.1. Again, variability from site to site and from parameter to parameter is noted. The results of bias and precision of measurements with replicate samplers can be compared with the mean concentration observed at the corresponding sites to render measurement uncertainty information at these sites. Similarly, normalized bias and

normalized precision for the same sampler types using equations (7) and (8) in Section 3.1 may be attempted to take into account the actual observations and yield information applicable to other sites. The results are given the Tables 5 and 6. As can be seen, the bias is small in general and its scatter (as precision) is moderate. The performance of the SES bulk samplers is better than that of Aerochem Metrics samplers in general.

The dependence of the precision on the concentration was also investigated, and found to be relatively small. For example, both the median and the 95-th percentile of the absolute percentage difference in co-located daily Aerochem Metrics samples were found to increase somewhat as the concentration decreased, but generally, values at the upper and lower concentration ranges were within a factor of two or so (c.f. Topol et al., 1982).

4.1.1.2 Cumulative Sampling

Colocation precipitation chemistry results over 28 d sampling intervals using Sangamo samplers are expressed in terms of median absolute difference in Table 7. Data include pooled results from all the participating stations and cover the period from late 1982 to October 1984, due to the fact that there was only a limited number of data pairs at each site.

For concentration measurements, reproducibility (one minus absolute difference) is better than 88% for acid-base parameters (H_t^+ , H_f^+ , $SO_4^{=}$, NO_3^- and NH_4^+). Both sample depth and gauge depth are reproducible to 95% or better. Parameters including other major ions (Ca^{++} , Cl^- , Mg^{++} and Na^+), trace metals, (Mn, Zn, Fe, Pb, Al, and Cu) and TKN are at least 75% reproducible. K^+ and PO_4^{-3} are the least reproducible parameters, being only 55% and 25% respectively. The reason for the former may be related to detection limit problem and the latter to instability.

Reproducibility of loading measurements for the acid-base parameters is somewhat worse than that of concentration measurements. For other parameters, it is somewhat improved or comparable to the concentration reproducibility.

Results for bias and precision are not given for the 28 d co-location sampling as there are so few data for each site.

4.1.2 Air Samplers

Tables 8 and 9 summarize results of median absolute difference, bias, precision, normalized bias and normalized precision for daily and 28-day air concentration measurements respectively. In the daily measurements using Metrex SAS 8-25 samplers, only acid-base related parameters are determined. In the cumulative measurements using Metrex AS-2 samplers, other major ions and trace metals are also analyzed. NH_4^+ is not determined in the cumulative network because the Whatman 40 pre-filter has a variable NH_4^+ background. In the case of Metrex SAS 8-25, reproducibility (one minus absolute difference) for all measured parameters is 90% or better. Normalized bias is less than 10% and normalized precision is less than 30%.

In the case of Metrex AS-2 samplers, SO_2 reproducibility is poorer than that of the daily measurements, while that of other acid-base related parameters is comparable. Reproducibility for trace metal measurements is typically better than 80% with Cu and Ni reproducibility being as low as 75%. Normalized bias and normalized precision were not determined due to the small sample size per site, but it is expected that they should follow a similar pattern qualitatively.

4.2 Sampler Equivalency

Co-located data collected at various sites on a daily basis with Aerochem Metrics, SES bulk and Sangamo samplers are analyzed to determine whether they are equivalent and by how much they were different.

Table 10 summarizes results of median absolute difference (equation (9) in Section 3.3) in concentration and loading measurements between different sampler types. Loading differences are in general higher than those of concentrations. Concentration differences between Sangamo and Aerochem Metrics samplers for acid-base related parameters (H_f^+ , H_t^+ , SO_4^- , NO_3^- , NH_4^+) are less than 14%, but for soil-related (Ca^{++} , Mg^{++} , K^+) and road salt related (Cl^- , Na^+) parameters are larger and amount up to 40% in some cases. Sample depth and sampling efficiency differences are less than 12%.

Median absolute differences for acid-base related species are, in general, higher between SES bulk and wet-only (Aerochem Metrics or Sangamo) samplers than the difference between the wet-only types. This is also true of sample precipitation depth and collection efficiency. Again, in the comparison between SES and wet-only samplers, it is noted that the concentration differences for soil- and road salt-related species are higher and that loading differences are higher than those of the concentration differences.

In order to examine the long term differences between sampler types, bias and precision (to be viewed as the standard deviation) results for concentration and loading for the 3 sampler comparisons are calculated and are given in Table 11. Among the three comparisons, the Sangamo vs. Aerochem comparison yields better agreement of concentration measurements whereas all three comparisons yield similar loading results. On average, over the same sampling interval, both Sangamo and SES bulk samplers have higher concentrations than the Aerochem Metrics samplers. This possibly reflects the fact that the sensor is less sensitive on the Aerochem Metrics sampler, resulting in missing collection of the initial portions of the precipitation event, which usually have higher concentrations. SES bulk sampler concentrations are higher or comparable to those of the Sangamo samplers. Bias in sample depth and collection efficiency indicates that the SES bulk sampler is the most efficient and the Sangamo sampler the least efficient in sample collection as a consequence of the size of the container openings (SES bulk Aerochem Metrics Sangamo). Sampler collection area is another factor besides sensor performance that affects the collection efficiency.

As a result of the combined effects of the differences of sensors and collection areas of the samplers, loadings of the SES bulk samplers are always higher than those of Aerochem Metrics and Sangamo samplers. There seems to be no systematic difference between the loadings of Sangamo and Aerochem Metrics samplers; it varies with the parameters being compared.

Quantitative differences of concentration and loading as observed by different samplers are evaluated by Bartlett linear regression analysis and the results are summarized in Tables 12 and 13. In both tables, n , r , S and I refer to the number of data pairs, linear correlation coefficient, slope and intercept respectively. Only those parameters with high correlation coefficients should be given attention. Those with low correlation coefficients suggest poorly defined relationships and therefore the determined slopes and intercepts carry little meaning.

In both tables, those slopes which are not different from unity and those intercepts which are not different from zero respectively at the 95% confidence level are labelled with an asterisk. It should be noted that both the slope and intercept information should be used in establishing the regression relationship between the two sampler types being considered. The slope can be used to assess the relative magnitude of the two measurements only if the intercept is not different from zero. The non-zero intercept indicates systematic differences between the two sampler types.

As shown in Table 12, the concentration results from different sampler types are highly correlated except in the case of potassium which is less significant between the SES and the wet-only samplers. With residuals being no different from zero, the regression of Aerochem Metrics (Y axis) results against those of Sangamo (X-axis) indicate that the Aerochem Metrics $\text{SO}_4^{=}$ and Ca^{++} concentrations are 6% and 22% lower than those of the Sangamo samples. This is consistent with the fact that the Sangamo sensor is more sensitive than the Aerochem Metrics' and allows collection of the initial, more concentrated subsamples of the precipitation events. All other concentration parameters with nonzero intercepts except NH_4^+ have a positive residual but they are small compared to the average concentration observed at those sites in Ontario. Slopes of all the concentration parameters are less than unity, typically 10% lower in the Aerochem Metrics results. Sample depth slope indicates about 8% higher collection by the Aerochem Metrics samplers than the Sangamo samplers. The increase in collection efficiency with the opening of collection vessels is substantiated by the observations on sample depth in the Aerochem Metrics and SES bulk sampler regression ($S=0.96$), Sangamo and SES bulk sampler regression ($S=0.88$) and Aerochem Metrics and Sangamo Sampler regression ($S=1.08$).

Residuals exist in the comparisons (see Table 12) of Sangamo vs. SES bulk and Aerochem Metrics vs. SES bulk samplers. The corresponding slopes indicate higher concentrations in the SES bulk samplers than both the Sangamo and Aerochem Metrics samplers. The differences agree qualitatively with those between the Aerochem and Sangamo samplers.

Table 13 gives results of loading comparisons. Because of the compensating effects between concentration and collection efficiency, loadings of the Aerochem Metrics and Sangamo samplers are more comparable. However, the loadings of the SES bulk sampler are higher than those of the Aerochem Metrics and Sangamo samplers.

4.3 Sampling Accuracy

This section describes results of experiments designed to estimate the accuracy of sampling on a cumulative (monthly or 28 d) basis and on a daily basis.

In order to isolate laboratory uncertainties and effects due to exposure of samples to atmospheric conditions (e.g. temperature and relative humidity), the standard solutions used in the study were portioned into four aliquots for the following purposes:

1. For measurements of initial concentrations
2. For storage in laboratory and analysis after a typical sampling period to check for potential changes under laboratory storage conditions.
3. For storage in a sealed sampling bag which was exposed to field conditions for the sampling interval.
4. For storage in an unsealed sampling bag in a sampler which was closed at all times during the sampling period under field conditions
5. For storage under field conditions in an unsealed polyethylene bag, in a sampler which was opened and closed upon contact of the sensor with moisture. However, while the standard solution was exposed to the atmosphere, precipitation did not enter into the bag, because the sampler (but not the sensor) was covered by a roof (see Figure 1). Sampling periods of 1 day and 28 days were examined.

The final concentrations in (2) to (5) were compared to the initial concentrations (1), as discussed in the following sections. As some of the sample concentrations were quite low, a criterion using 2 times the standard deviation of within-run duplicates was used to ensure that the difference between the initial and final concentrations is significant at the 95% confidence level. A summary of the within-run duplicates of the parameters of interest is given in Table 14.

4.3.1 Cumulative Precipitation Sampling

4.3.1.1 Samples in Laboratory During a Typical Sampling Period (2).

A comparison was made of the initial concentration and the final concentration of samples stored in the laboratory for a 28 d period in terms of their ratio. For cases with a difference less than 2 times the standard deviation of the within-run duplicates, the ratio is replaced by 1. Table 15 gives the ratios of the final to the initial concentrations. The initial concentration value represents the mean value of triplicate analyses whereas the final concentration entries correspond to the individual results obtained with three samplers. Except for very few cases, all the ratios are unity. The average observation is described by the median of the observed ratios ($n=15$). The median ratios are unity for all the parameters of interest, suggesting that storage under laboratory conditions brings about little changes to the sample.

4.3.1.2 Sealed Samples Stored Under Field Conditions Over a Sampling Period (3)

Similar to the approach described above in Section 4.3.1.1, ratios of final to initial concentrations are calculated of samples sealed but exposed to field conditions inside a precipitation collector. These ratios are given in Table 16. Ammonium concentrations fluctuate over the exposure period, indicating that ammonium is not an environmentally stable species. The median C_f/C_i ratio of N-NH_4^+ is one. The corresponding median ratio for $\text{SO}_4^{=}$ suggests that there is a small increase in $\text{SO}_4^{=}$ in the long run. Potassium and Cl^- increased over the storage period with median ratios of 1.28 and 1.11 respectively. Chloride could not be originated from NaCl contamination as the corresponding Na concentration was not elevated. Knowing that K^+ and Cl^- are chemically conservative, the difference is attributed to desorption from the polyethylene/nylon laminated bags. This speculation is qualitatively supported by some quality assurance results of experiments testing the sorption properties of these bags. It should be noted that the changes in K^+ and Cl^- concentrations are usually small compared to the concentrations observed of the network samples.

Most of these samples were exposed under spring/summer conditions where temperature changes could be extreme. The results indicate that aside

from K^+ and Cl^- (which suffered from bag desorption), all parameters, except $SO_4^{=}$ which seemed to increase slightly, were not affected at all upon exposure to field conditions for a typical sampling period.

4.3.1.3 Unsealed Samples Stored in a Closed Sampler Under Field Conditions (4)

The evaporative effect can be estimated by examining the ratios of final-to-initial sample volumes. These results are given in Table 17. For each period, there were 3 samples (typically with an initial volume of 500 ml each) used in the experiment and their corresponding results were usually quite consistent. Evaporation losses typically amount to about 60 cc per 28 days in the spring; 130 cc in the summer; 40 cc in the autumn; and about 10 cc during winter. The corresponding actual precipitation volumes collected for the above four seasons at Dorset (for a 28 d period) are typically 1.8, 2.6, 2.8 and 1.6 litres. Therefore, expressed as a seasonal percentage, evaporation losses are estimated to be 3%, 5%, 1.4% and 0.6% for the spring, summer, fall and winter respectively, and about 3% as an annual average. It should be noted that as of the summer of 1984 (after the above experiments were carried out) the sampler lid gaskets were changed to improve the lid seal, and recent tests indicate that evaporative losses are currently a small fraction of what they were with the pre-summer of 1984 design, i.e, about 1% or less.

4.3.1.4 28-Day Unsealed but Sheltered Samples (5)

In this experiment, a change in sample concentration over the study period could be due to both evaporation and dry deposition. The former can be accounted for by the ratio of the final-to-initial sample volumes.

In order to estimate the dry deposition contribution, the observed concentrations after the period were scaled by multiplying with the ratio of final-to-initial volumes and the corrected final concentrations were then compared with the initial ones. These ratios are summarized in Table 18. Some of the extreme values were due to the extremely small initial or final values.

As pointed out before, NH_4^+ is environmentally unstable and its fluctuation is not unexpected. Potassium and chloride may suffer from bag

surface desorption. The median ratios indicate that over the long term, dry deposition has little effects on H_t^+ , H_f^+ , $SO_4^{=}$, NO_3^- and Na. However, the dry deposition contribution of soil-related parameters is observable and could be as high as 11% for Ca^{++} and 31% for Mg^{++} .

4.3.2 Daily - Unsealed but Sheltered Samples

Standard samples were exposed under the above condition of a 24 h period on days with or without precipitation. The results are given in Table 19.

An analysis of the final-to-initial sample volumes indicates evaporation over 1 day was negligible and was rarely greater than 1% which is the accuracy of the weighing scale. A comparison of the final-to-initial concentrations of over 200 samples suggests none of the parameters of interest was, on average (indicated by the median ratio), affected by dry deposition over a 1 d period. In terms of individual precipitation sample collections, there were times when dry deposition was observable, as indicated by high soil-related parameter concentrations. This is consistent with the observations made in another study (Chan et al., 1984). These results indicate that the sampling error in daily wet-only precipitation chemistry by Aerochem Metrics samplers, on average, is small and is within the laboratory precision.

4.4 Equivalency of Daily and 28d Sampling Protocols

4.4.1 Cumulative (Sangamo Sampler) and Daily Accumulated (Aerochem Metrics)

Evaluations of the effects of sampling intervals up to two weeks on wet deposition monitoring have been made by Madsen (1982) and de Pena et al. (1985) using simple statistical analysis methods. Conclusions drawn from these studies are not consistent with each other. In this study, an extended assessment is made of the equivalency of daily (Aerochem Metrics) vs. cumulative (monthly or 28d Sangamo sampling). An elucidation of the origin of the discrepancies is also attempted.

Concentrations of Sangamo cumulative samples (monthly or 28 days) were compared with precipitation depth weighted concentrations of Aerochem Metrics daily samples accumulated over the same cumulative sampling periods. Similarly, the accumulated deposition values of the daily samples over the same interval are compared to those of the cumulative samples. In the following section, the equivalency will be assessed in terms of Bartlett linear regression analysis, median absolute difference, bias and normalized bias. The results are further analyzed to evaluate the effects of evaporation and mechanical efficiency differences.

4.4.1.1 Regression Analysis

Table 20 gives Bartlett linear regression results using the original (uncorrected) cumulative data. Correlation is statistically significant at the 95% confidence level for all concentration, deposition and loading parameters. The correlation is lowest for K^+ and there is a positive residual in the cumulative concentrations and deposition. In the cases where the intercepts are no different from zero, the cumulative concentrations are either no different from (H_t^+ , H_f^+ , NO_3^-), greater than ($SO_4^{=}$, NH_4^+ , Ca^{++} and Mg^{++}) or less than (Na^+ and Cl^-) those of the accumulated daily samples. It is surprising that gauge depths (daily AES standard gauge or Nipher-shielded gauge vs. 28 d storage gauge) are not equivalent while the sample depths are. The equivalency of sample depths indicates little evaporation. The higher cumulative sample concentrations (Ca^{++} and Mg^{++}) can be attributed to potential dry deposition over the 28 d period and also the better sensitivity of the Sangamo sensor. However, the lower concentrations (Na^+ , Cl^- and K^+) are not as readily understood. Correlation is improved in general for both the deposition and loading results. The above observations on concentration results also in general apply to deposition with the exception that H_f^+ intercept is non-zero. The slopes in the loadings regression are lower than those of concentration and deposition.

Table 21 summarizes regression results with data after evaporation corrections by using the ratio of cumulative sample depth to the daily gauge depths. Correlation is comparable to but somewhat worse than that without correction, but the slopes indicate overcorrection. Again, this supports the contention that evaporation cannot solely explain the difference in cumulative and accumulated daily sample concentrations.

4.4.1.2 Median Absolute Difference, Bias and Normalized Bias

In order to quantify the difference between the cumulative measurements and the accumulated daily measurements, the absolute difference and bias are calculated. Results are given in Table 22. The median absolute difference between the cumulative and accumulated daily samples is less than 12% for H_t^+ , H_f^+ , $SO_4^{=}$, NO_3^- , Cl^- and NH_4^+ but is higher for Ca^{++} , Mg^{++} , K^+ and Na^+ , up to 22%. Results are similar for the loading and deposition comparisons. Normalized bias for H_t^+ , H_f^+ , $SO_4^{=}$, NO_3^- , Mg^{++} and NH_4^+ is less than 10% and is higher for Ca^{++} , indicating higher cumulative concentrations than the accumulated daily concentrations. Chloride, K^+ and Na^+ have negative bias which is consistent with the observations made in Section 4.4.1.1. Sample and gauge depths also show negative bias suggesting lower Sangamo collection efficiency.

4.4.1.3 Collection Efficiency and Evaporation

Based on the formulation given in Section 3.3, five different ratios using accumulated daily (Aerochem Metrics) and cumulative (Sangamo) sampling results are given in Tables 23 and 24.

From Table 23, it is seen that sample depth of the cumulative sample is on the order of 20% less than the accumulated daily samples throughout the year. This is a combined effect of evaporation and less than 100% collection efficiency of the Sangamo samplers. The reported ratio of cumulative sample depth to the accumulated daily sample depth is equal to the product of collection efficiency and retention efficiency after evaporation (McRc). The McRc ratios remain quite constant throughout the summer months (May to October) and winter months (November to April) but are somewhat lower in the winter periods. At this point, we can make use of the results in Section 4.3.1.3 on evaporation losses ($R_c = 0.95, 0.99$ and 0.97 for the summer, winter and annual averages respectively) to determine the corresponding collection efficiency (M_c) values: 0.85 (summer), 0.75 (winter) and 0.80 (annual average).

There is a small difference in the standard gauge depths in Table 23 for both the cumulative and accumulated daily sampling throughout the year, being about 5% less in the cumulative gauge depth. This suggests that the deposition (i.e. concentration x gauge depth) difference in the two types of sampling depends mainly on the concentration difference.

Results in Table 24 yield independent information on the difference in collection efficiency (M_c), evaporative effects ($1-R_c$) and the difference in calculated deposition using cumulative and accumulated daily samples based on acid/base-related parameters. Due to the potential for sample contamination, and larger laboratory analysis errors, results for other major ions have a somewhat higher scatter. The following discussion will be based on Table 24 only.

The scatter in the acid/base results is not large, typically with a coefficient of variation (std. dev./mean) less than 30%. Results for H_f^+ , H_t^+ , $SO_4^{=}$, NO_3^- and NH_4^+ are quite consistent. Using just these acid-base related parameter results, the difference due to collection efficiency is 12%, evaporation is 9% (c.f. 3% in Section 4.3.1.3), and the net deposition overestimation in the cumulative sample is 12% (due partly to a compensation of errors). The difference in deposition may be partially due to the fact that there are missing results of daily samples with insufficient volume for complete chemical analysis and the evaporative loss may also reflect the missing initial fractions of precipitation samples which are usually more concentrated (Raynor and Hayes, 1981) by the Aerochem Metrics samplers due to sensor insensitivity.

The results of the evaporation loss and collection efficiency assessment on the cumulative network may be summarized as follows: in the pre-1984 network, evaporation losses were about 3-10% of the final sample volume, with the direct tests of evaporation (Section 4.3.1.3) favoring the lower values. If a standard gauge is used to determine deposition (as in the APIOS network), then the evaporation losses would introduce positive errors of the same order (3-10%) in the deposition values. The annual average collection efficiency in the APIOS cumulative network is in the 80-90% range (somewhat higher in summer than winter), but if the collection efficiency is constant throughout each event, and a standard gauge is used to determine deposition, then there should be no resulting error in the deposition values due to less-than-100% collection efficiency.

4.4.2 Cumulative (Metrex AS-2 Sampler) and Daily (Metrex SAS 8-25) Air Filter Pack Sampling

4.4.2.1 Regression Analysis

Table 25 summarizes the Bartlett linear regression analysis results. Due to the different filter arrangements in the daily and 28d sampling schemes and the potential of artifact NO_3^- formation, it is appropriate to compare only the total N-NO_3^- rather than N-NO_3^- (particulate) and N-HNO_3 separately. There is a small residual in SO_2 and total N-NO_3^- . The SO_2 and $\text{SO}_4^{=}$ concentration results are similar in both types of sampling whereas there is about 17% less total N-NO_3^- in the daily sampling with teflon-nylon filter arrangement than the 28d sampling with Whatman 40 - nylon filter arrangement.

Even though both SO_2 and total N-NO_3^- have non-zero intercept, the total N-NO_3^- intercept is minimal. There is some indication of residual SO_2 in the 28d lo-vol sampling scheme and it may be related to the unaccounted for SO_2 adsorption on the nylon filter. From an examination of the air sampling data, it is recognized that, depending on the ambient SO_2 concentration, the amount of SO_2 adsorbed on the nylon filter with respect to the SO_2 trapped on the K_2CO_3 impregnated Whatman 41 filter varies. There appears a saturation effect. In our comparison results given in Table 25, the nylon SO_2 (determined as $\text{SO}_4^{=}$) has not been taken into account. As a result of the saturation effect, one would expect the impact be greater in the summation of daily samples than a single 28d sample.

4.4.2.2 Median Absolute Difference, Bias and Normalized Bias

In order to quantify the difference of the 2 types of measurement technique/period, the air sampling results are expressed in Table 26 as normalized absolute difference, bias and normalized bias.

The difference and normalized bias between the two schemes is typically less than 13% for SO_2 and less than 5% for $\text{SO}_4^{=}$ and NO_3^- . The SO_2 results also indicate more loading in the 28d lo-vol scheme, consistent with the results in Table 25.

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TABLE 1
Results of Median Absolute Percentage Difference of Daily Precipitation Chemistry Measurements
by a Pair of Aerochem Metrics Samplers*

Parameter	Longwoods			n	Dorset		n	Railton		n	All Stations	
	n**	C	L		C	L		C	L		C	L
H _t ⁺	130	4.19	4.80	186	4.51	6.77	16	6.77	16.32	332	4.51	5.95
H _f ⁺	136	6.91	6.91	195	6.91	10.14	14	11.54	19.49	345	6.91	8.55
SO ₄ ⁼	142	2.67	3.52	195	3.64	5.57	15	5.80	12.98	352	3.39	4.90
N-NO ₃ ⁻	142	2.74	3.79	192	3.05	6.00	15	10.72	16.04	349	2.99	5.05
Ca ⁺⁺	122	15.90	14.94	150	11.41	11.87	13	20.73	30.65	285	13.39	13.08
Cl ⁻	139	11.15	12.17	179	12.17	13.80	12	8.23	40.34	330	11.81	13.02
Mg ⁺⁺	122	15.48	13.97	135	0.00	7.39	11	75.00	59.56	268	10.05	10.32
K ⁺	119	25.87	24.70	133	22.50	22.50	12	29.17	37.89	264	22.50	23.90
Na ⁺	121	22.50	22.32	143	13.9	15.40	9	0.00	10.14	273	15.48	18.23
N-NH ₄ ⁺	122	5.60	5.82	152	6.74	8.23	15	3.24	14.24	289	6.22	7.52
SDP	161	2.08	-	219	3.18	-	16	8.34	-	396	2.79	-

* See Section 3.1 for definitions and formulations; H_t^+ = total hydrogen, H_f^+ = free hydrogen, n = number of data pairs, C = Concentration; L = Loading and SDP = sample depth

** The number of data pairs used for the L calculations may be slightly less than that for the C calculations.

TABLE 2
Results of Median Absolute Percentage Difference of Daily Precipitation Chemistry
Measurements by a Pair of SES Bulk Samplers*

Parameter	Longwoods			Dorset			Charleston Lk			All Stations		
	n	C	L	n	C	L	n	C	L	n	C	L
H_t^+	17	7.31	11.22	24	2.94	4.67	51	4.56	5.34	92	4.53	6.03
H_f^+	11	4.61	8.11	38	5.76	6.46	58	4.61	7.58	107	4.62	6.92
$SO_4^{=}$	19	3.62	8.11	38	2.00	2.53	66	1.47	3.36	123	1.84	3.39
$N-NO_3^-$	20	2.64	6.56	38	1.47	2.30	65	2.20	3.54	123	2.06	3.38
Ca^{++}	12	18.61	18.36	32	7.16	6.55	56	10.86	13.24	100	11.11	12.13
Cl^-	17	19.80	18.25	39	10.03	9.78	63	3.18	5.66	119	6.67	7.75
Mg^{++}	12	12.46	7.62	31	0	2.79	55	11.81	13.91	98	7.72	8.07
K^+	18	39.64	25.52	32	19.27	17.80	60	2.70	11.16	110	16.13	17.80
Na^+	18	15.57	21.29	33	9.55	10.40	59	3.77	6.65	110	6.26	10.15
$N-NH_4^+$	17	3.77	5.71	37	4.35	4.05	64	4.02	4.42	118	4.09	4.55
SDP	21	5.38	-	45	1.87	-	70	2.20	-	136	2.20	-

* See Section 3.1 for definitions and formulations; n = number of data pairs, C = Concentration; L = Loading and SDP = sample depth

TABLE 3
Results of Bias and Precision of Daily Precipitation Chemistry (Concentration)
Measured by a Pair of Aerochem Metrics Samplers*

Parameter	n**	Longwoods		n	Dorset		n	Railton	
		B	P		B	P		B	P
H_t^+	130	0.001	0.019	186	0.002	0.021	16	-0.003	0.007
H_f^+	136	-0.002	0.010	195	0.001	0.008	14	-0.002	0.004
$SO_4^{=}$	142	-0.036	0.419	195	0.068	0.394	15	-0.067	0.160
$N-NO_3^-$	142	-0.005	0.068	192	0.004	0.090	15	-0.013	0.048
Ca^{++}	122	0.003	0.120	150	0.001	0.031	13	0.003	0.041
Cl^-	139	-0.003	0.063	179	0.002	0.056	12	-0.011	0.026
Mg^{++}	122	0.000	0.022	135	-0.001	0.008	11	-0.002	0.007
K^+	119	-0.005	0.034	133	0.001	0.024	12	-0.000	0.011
Na^+	121	-0.001	0.034	143	0.003	0.023	9	0.007	0.017
$N-NH_4^+$	122	-0.003	0.070	152	0.003	0.036	15	-0.011	0.027
SDP	161	-0.136	0.913	219	0.044	0.651	16	-0.118	3.785
GDP	184	0.003	0.066	273	-0.011	0.103	21	0.324	0.975

* n = number of data pairs; SDP = sample depth; GDP = gauge depth; B = Bias;
P = Precision
(see Section 3.1 for formulations)

** The number of data pairs used for the L calculations may be slightly less than that for the C calculations.

TABLE 4
Results of Bias and Precision of Daily Precipitation Chemistry (Concentration)
Measured by a Pair of SES-Bulk Samplers*

Parameter	n	Longwoods		n	Dorset		n	Charleston Lk	
		B	P		B	P		B	P
H_t^+	17	-0.003	0.009	24	-0.003	0.011	51	-0.001	0.008
H_f^+	11	-0.001	0.008	38	-0.001	0.008	58	0.000	0.006
$SO_4^{=}$	19	-0.026	0.262	38	0.008	0.155	66	-0.002	0.196
$N-NO_3^-$	20	0.016	0.096	38	0.002	0.029	65	0.009	0.121
Ca^{++}	12	-0.002	0.162	32	-0.001	0.037	56	-0.026	0.106
Cl^-	17	0.000	0.061	39	-0.005	0.040	63	0.002	0.048
Mg^{++}	12	-0.003	0.028	31	-0.000	0.004	55	-0.005	0.016
K^+	18	-0.018	0.061	32	-0.009	0.027	60	-0.003	0.024
Na^+	18	-0.017	0.066	33	-0.015	0.050	59	0.006	0.078
$N-NH_4^+$	17	0.007	0.063	37	-0.006	0.026	64	0.001	0.040
SDP	21	-4.84	2.205	45	0.033	0.206	70	-0.341	1.950

* n = number of data pairs; SDP = sample depth; B = Bias; P = Precision
(see Section 3.1 for formulations)

TABLE 5

Results of Normalized Bias and Normalized Percentage Precision of Daily Precipitation Chemistry Measurements
by a Pair of Aerochem Metrics Samplers

Parameter	n**	Longwoods		n	Dorset		n	Railton	
		BP	PP		BP	PP		BP	PP
H _t ⁺	130	0.89	20.84	186	1.37	13.66	16	-11.60	24.94
H _f ⁺	136	-0.14	26.53	195	2.49	22.48	14	-8.29	13.66
SO ₄ ⁼	142	-0.06	12.22	195	2.08	12.27	15	-8.52	15.04
N-NO ₃ ⁻	142	0.54	12.25	192	1.46	16.54	15	-7.10	17.82
Ca ⁺⁺	122	-0.99	32.56	150	3.93	26.52	13	14.24	32.50
Cl ⁻	139	-1.41	29.19	179	-0.48	31.02	12	-5.46	40.96
Mg ⁺⁺	122	-1.33	35.07	135	0.48	30.10	11	-2.18	55.59
K ⁺	119	-5.46	45.68	133	5.22	44.33	12	10.68	42.35
Na ⁺	121	-3.18	44.11	143	4.31	36.63	9	13.11	45.48
N-NH ₄ ⁺	122	-1.98	18.03	152	2.13	18.31	15	-5.45	16.76
SDP	161	-2.19	13.81	219	-0.82	11.84	16	-7.51	31.64
GDP	184	0.09	1.02	276	-0.03	12.50	21	5.58	12.83

* n = number of data pairs; SDP = sample depth; GDP = gauge depth; BP = Percentage normalized bias; PP = Percentage normalized precision (see Section 3.1 for formulations)

** The number of data pairs used for the L calculations may be slightly less than that for the C calculations.

TABLE 6
Results of Normalized Bias and Normalized Percentage Precision
of Daily Precipitation Chemistry Measurements by a Pair of SES Bulk Samplers

Parameter	Longwoods			Dorset			Charleston Lk		
	n	BP	PP	n	BP	PP	n	BP	PP
H_t^+	17	-2.35	10.10	24	0.98	5.50	51	-0.49	5.02
H_f^+	11	-3.43	6.12	38	0.34	5.73	58	0.69	13.72
$\text{SO}_4^{=}$	19	-0.88	5.70	38	0.38	2.84	66	-0.55	5.79
N-NO_3^-	20	0.043	3.74	38	0.46	3.15	65	-0.20	6.53
Ca^{++}	12	4.00	13.64	32	3.08	19.65	56	-0.60	18.14
Cl^-	17	3.00	10.63	39	-0.27	10.59	63	0.39	17.53
Mg^{++}	12	2.15	10.79	31	0.46	11.86	55	-0.08	15.68
K^+	18	-5.08	33.02	32	-9.59	26.26	60	-1.47	23.16
Na^+	18	-2.20	23.15	33	-5.33	19.93	59	0.23	17.67
N-NH_4^+	17	0.78	5.48	37	-2.32	15.57	64	0.76	11.15
SDP	21	-0.74	6.52	45	0.14	3.37	70	-0.86	5.75

* n = number of data pairs; SDP = sample depth; BP = Percentage normalized bias;
PP = Percentage normalized precision (see Section 3.1 for formulations)

TABLE 7

Results of Median Absolute Percentage Difference of 28d Precipitation Measurements
by a Pair of Sangamo Samplers*

Parameter ⁺	n	C	n	L	Parameter	n	C	n	L
H _t ⁺	49	9.18	42	12.36	TKN	50	12.84	43	12.29
H _f ⁺	49	11.54	42	14.19	PO ₄ ³⁻	47	75.00	41	48.75
SO ₄ ⁼	50	6.14	43	10.24	Mn	50	11.81	43	9.6
N-NO ₃ ⁻	49	5.13	42	7.48	Zn	47	23.61	41	22.67
Ca ⁺⁺	50	12.60	43	14.41	Fe	47	23.87	41	25.29
Cl ⁻	50	13.39	43	14.49	Pb	50	25.83	43	29.17
Mg ⁺⁺	50	21.35	43	20.82	Al	47	22.03	41	25.79
K ⁺	44	45.21	38	41.67	Cu	47	12.47	41	10.49
Na ⁺	48	23.95	41	20.14					
N-NH ₄ ⁺	48	12.28	41	16.11					
SDP	48	5.15	-	-					
GDP	44	4.31	-	-					

* C = concentration and L = loading.

+ Results are not given for Ni, V and Cd as most of the analytical results are at the detection limit.

TABLE 8
Performance of Daily Sampler for Air Concentration Measurements
at Dorset (Jan.-June, 1984)*

Parameter	n	D	B	P	BP	PP
SO ₂	114	10.13	4.51	37.60	2.08	25.59
SO ₄ ⁼	119	5.65	1.10	15.87	0.05	26.65
N-NO ₃ ⁻	46**	8.72	0.02	0.66	8.98	28.57
N-HNO ₃	116	7.16	-0.41	1.07	-4.10	16.80
N-NH ₄ ⁺	119	5.24	0.37	2.48	6.43	30.44

* n= number of data pairs; D = median absolute percentage difference;
 B = Bias; P = Precision; BP = normalized bias and PP = normalized precision

** 65 pairs of (0,0) data not used in statistics

TABLE 9
Performance of Cumulative Air Sampler (Jan.-Jun.,1984)

Parameter	n	D*	Parameter	n	D*
SO ₂	28	14.95	Al	27	6.69
SO ₄ ⁼	26	6.21	Mg ⁺⁺	27	7.65
N-HNO ₃	27	5.88	Pb	27	12.83
N-NO ₃ ⁻	26	6.95	Mn	27	10.72
Ca ⁺⁺	27	12.47	Cu	27	25.30
Cl ⁻	26	8.41	Ni	27	22.74
K ⁺	27	19.64	V	27	8.27
Na ⁺	27	7.42	Zn	27	16.00
Fe	27	10.95	Cd	27	16.78

* D = median normalized absolute difference

TABLE 10
Results of Median Absolute Percentage Difference of Daily Precipitation Chemistry
Measurements by a Pair of Different Samplers*

Parameter	Sangamo vs. Aerochem			SES vs. Aerochem			SES vs. Sangamo		
	n	C*	L*	n	C	L	n	C	L
H_t^+	146	7.99	11.99	365	11.71	23.52	77	8.54	16.05
H_f^+	299	13.79	16.96	472	18.37	31.59	204	13.79	22.57
$SO_4^{=}$	282	8.81	13.73	482	19.32	32.22	196	11.43	18.41
$N-NO_3^-$	293	9.09	14.22	488	15.56	29.96	199	8.00	18.40
Ca^{++}	189	27.03	24.12	327	40.00	50.33	111	28.57	35.81
Cl^-	278	20.34	27.19	463	22.22	34.24	190	14.63	22.71
Mg^{++}	188	21.46	20.23	313	40.00	52.31	115	38.46	43.96
K^+	187	40.00	38.72	374	40.00	38.76	115	40.00	39.87
Na^+	184	40.00	45.96	366	34.05	38.82	117	25.00	28.34
$N-NH_4^+$	215	12.01	14.19	376	21.72	29.62	139	11.97	-
SDP	345	11.71	-	590	16.19	-	241	12.98	-
Eff	338	11.58	-	560	17.25	-	219	14.57	-

* SDP = Sample Depth; Eff = Sampling Efficiency; C = Concentration and
L = Loading

TABLE 11
Results of Sampling Bias and Precision Between Two Different Precipitation Sampler Types*

Parameter	Sangamo vs. Aerochem					SES vs. Aerochem					SES vs. Sangamo				
	C		L		n	C		L		n	C		L		n
	B	P	B	P		B	P	B	P		B	P	B	P	
H _t ⁺	146	0.001	0.016	-0.085	0.284	385	0.007	0.033	0.067	0.256	77	-0.001	0.019	0.127	0.267
H _f ⁺	299	0.003	0.022	-0.015	0.175	472	0.006	0.024	0.056	0.164	204	-0.001	0.024	0.052	0.166
SO ₄ ⁼	282	0.273	0.753	-0.343	7.975	482	0.640	1.272	3.624	6.110	196	0.220	1.027	3.989	6.453
N-NO ₃ ⁻	293	0.056	0.149	0.040	1.338	488	0.120	0.257	0.786	1.240	199	0.027	0.191	0.682	1.293
Ca ⁺⁺	189	0.057	0.139	0.343	1.644	327	0.120	0.253	0.820	1.838	111	0.074	0.260	1.049	2.483
Cl ⁻	278	0.007	0.110	-0.082	0.645	463	0.026	0.149	0.184	0.800	190	-0.001	0.089	0.194	0.600
Mg ⁺⁺	188	0.005	0.018	0.010	0.200	313	0.019	0.045	0.112	0.406	115	0.014	0.054	0.141	0.540
K ⁺	187	0.004	0.025	-0.002	0.316	374	0.004	0.053	0.067	0.353	115	-0.004	0.030	0.020	0.254
Na ⁺	184	-0.004	0.057	-0.094	0.507	366	0.008	0.121	0.064	0.538	117	-0.000	0.064	0.136	0.529
N-NH ₄ ⁺	215	0.027	0.082	-0.011	1.324	396	0.079	0.149	0.486	0.925	139	0.016	0.133	0.487	1.215
SDP	345	-0.496	1.783	-	-	590	0.505	1.294	-	-	241	0.713	1.399	-	-
Eff.	338	-0.378	23.170	-	-	560	23.079	46.157	-	-	219	13.003	31.096	-	-

* SDP = sample depth; Eff. = collection efficiency; C = Concentration; L = Loading; B = Bias and P = Precision (see Section 3.1 for formulations).

TABLE 12

Bartlett Linear Regression Results of Daily Precipitation Chemistry Determined by Different Sampler Types**

Parameter	Sangamo vs. Aerochem				SES vs. Aerochem				SES vs. Sangamo			
	n	r	S	I	n	r	S	I	n	r	S	I
H_t^+	146	0.97	0.898	0.010	383	0.81	0.691	0.021	77	0.89	0.838	0.015
H_f^+	299	0.96	0.907	0.005	491	0.90	0.777	0.011	204	0.93	0.905	0.008
$SO_4^{=}$	282	0.97	0.943	-0.500*	509	0.91	0.764	0.209	196	0.94	0.879	0.215
$N-NO_3^-$	293	0.96	0.870	0.029	515	0.90	0.751	0.061	199	0.94	0.924	0.028
Ca^{++}	189	0.91	0.779	0.008*	343	0.81	0.509	0.032	111	0.81	0.671	0.062
Cl^-	278	0.83	0.895	0.014	489	0.76	0.682	0.050	190	0.88	0.889	0.026
Mg^{++}	188	0.96	0.825	0.003	332	0.73	0.521	0.005	115	0.73	0.700	0.005
K^+	187	0.72	0.676	0.008	400	0.34	0.446	0.020	115	0.50	0.609	0.018
Na^+	184	0.74	0.909	0.009	390	0.59	0.619	0.032	117	0.81	0.851	0.014
$N-NH_4^+$	215	0.96	0.974	-0.017	399	0.88	0.744	0.020	139	0.92	0.907	0.021
SDP	345	0.99	1.084	-0.175	618	0.94	0.957	-0.064*	241	0.99	0.883	0.070*
GDP	351	0.99	0.998*	0.028*	715	0.99	0.990	0.147	263	1.00	0.989	0.167

* At the 95% confidence level, S (Slope) is no different from unity or I (Intercept) is no different from zero

** SDP = sample depth GDP = gauge depth, r = corr. coeff., n = no. of values, S = slope, I = intercept

TABLE 13

Bartlett Linear Regression Results of Wet Loadings Determined by Different Sampler Types

Parameter	Sangamo vs. Aerochem				SES vs. Aerochem				SES vs. Sangamo			
	n	r	S	I	n	r	S	I	n	r	S	I
H_t^+	146	0.97	1.035	0.038	372	0.91	0.939	0.003*	73	0.96	0.848	0.069
H_f^+	293	0.97	1.020	0.002*	473	0.92	0.865	0.012	187	0.96	0.826	0.028
$SO_4^{=}$	277	0.98	1.053	-0.827	491	0.85	0.830	0.768	177	0.98	0.843	0.122*
$N-NO_3^-$	288	0.96	1.010	-0.088*	497	0.73	0.841	0.026*	180	0.97	0.838	0.078*
Ca^{++}	187	0.89	0.849	0.116*	331	0.63	0.478	0.186	100	0.88	0.614	0.521
Cl^-	273	0.86	1.016	0.062	472	0.53	0.739	0.203	173	0.92	0.778	0.118
Mg^{++}	186	0.95	0.942	0.017	322	0.61	0.564	0.024	104	0.79	0.714	0.033*
K^+	185	0.78	0.861	0.060	387	0.51	0.509	0.089	104	0.76	0.536	0.150
Na^+	182	0.69	0.895	0.149	377	0.45	0.694	0.198	106	0.88	0.740	0.112
$N-NH_4^+$	211	0.97	1.035	-0.147	384	0.97	0.880	-0.193	123	0.98	0.859	0.102*

* At the 95% confidence level, S (Slope) is no different from unity or I (Intercept) is no different from zero.

TABLE 14
Within-run Duplicate Analysis Results

	Conc. range (mg l ⁻¹)	2 x Std. Dev.		
		1982	1983	1983
H _f ⁺	0-0.04			0.0088
	0.04-0.25			0.0130
	.25-.5			0.0060
	.5-1			0.0028
pH	3-4	0.080	0.028	0.058
	4-5	0.052	0.076	0.242
	5-6	0.108	0.140	0.208
SO ₄ ⁼	0-2	0.086	0.088	0.078
	2-5	0.166	0.128	0.146
	5-10	0.200	0.232	0.214
N-NO ₃ ⁻	0-0.4	0.020	0.028	0.032
	0.4-1	0.038	0.026	0.044
	1-2	0.032	0.162	0.076
Ca ⁺⁺	0-0.4	0.046	0.026	0.022
	0.4-1.0	0.070	0.092	0.056
	1.0-2.0	0.058	0.014	0.042
C ₁ ⁻	0-0.3	0.040	0.038	0.042
	0.3-0.75	0.042	0.050	0.036
	0.75-1.50	0.038	0.132	0.066
Mg ⁺⁺	0-0.1	0.0086	0.0100	0.0090
	0.1-0.25	0.0226	-	0.0084
	0.25-0.5	0.0156	0.0058	0.0186
K ⁺	0-0.2	0.016	0.012	0.014
	0.2-0.5	0.028	-	0.026
	0.5-1	0.088	-	0.014
Na ⁺	0-0.2	0.024	0.012	0.014
	0.2-0.5	0.012	-	0.008
	0.5-1	0.026	-	-
N-NH ₄ ⁺	0-0.1			0.0068
	0.1-0.5			0.0152
	0.5-1			0.0248
	1-2			0.0502

Summary of Ratios of Final-to-Initial Concentrations of Samples Stored under Laboratory Conditions over a 28 d Period

Final Concentration/Initial Concentration

[illegible]

TABLE 16
Summary of Ratios of Final-to-Initial Concentrations of Sealed
Samples Exposed to Field Condition over 28 Days

<u>Date</u> <u>Initial/Final</u>	<u>Final Concentration/Initial Concentration</u>									
	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	H _f ⁺	H _t ⁻	Cl ⁻	N-NO ₃ ⁻	SO ₄ ⁼	N-NH ₄ ⁺
820330/0427	1	1	1	1	1	1	1.11	1	1	1.22
"	1	1	1	1	1.01	1	1.11	1	1	1.25
"	1	1	1	.68	1.02	.82	1.11	1	1	2.52
820427/0523	1	1	1	1.16	.97	1	-	-	-	1.07
"	1	1	1	1.16	.95	1	-	-	-	1
"	1	1	1	1.28	.95	1	-	-	-	1
820525/0622	1	1	1	.86	.97	1.11	1.05	1	1.03	1
"	1	1	1	1.29	1	1.03	1	1	.99	1
"	1	1	1	1	1	1.08	1	1	.93	1
820622/0720	1	1	1.55	1.4	.96	1.86	1.19	1	1	1.07
"	1	1	1	1.3	.95	2.03	1.22	1	1.04	1.07
"	1	1	1	1.3	.98	1.30	1.10	1.09	1.04	1
820720/0817	1	1	1	1.56	1	1.15	1	1	1.03	.85
"	1	1	1	1.56	1	1.16	1	1	1.04	.80
"	1	1	1	1.56	1	1.17	1.33	1	1.06	.90
n	15	15	15	15	15	15	12	12	12	15
median	1	1	1	1.28	1	1.08	1.11	1	1.03	1

TABLE 17
A Comparison of Final-to-Initial Volumes of Samplers
Unsealed but Covered upon Exposure to
Field Condition over 28 days.

<u>Sampling Date</u>		<u>V_f/V_i</u>
83	05 24	.98, .78, .81,
	06 22	.78, .68, .74,
	07 19	.51, .74, .53,
	08 16	.73, .79, .66,
	09 13	.71, .72, .79,
	10 11	.81, .86, .88,
	11 08	.95, .95, .95,
	12 06	.96, .97, .97,
	84 01 03	.99, .99, .98,
	01 31	.99, .99, .99,
	02 28	.97, .99, .96,
	03 27	.93, .96, .96,
	04 24	.85, .93, .88,
	05 22	.77, .80,
	06 19	.71, .84, .74,
	07 17	.69, .83, .88,
	08 14	.63, .83, .86,
	09 11	.75, .78, .77,
	10 09	.90, .89, .89,
	11 06	.88, .93, .92,
Spring (Mar - May)		n = 11 .88 ± .08
Summer (Jun - Aug)		n = 24 .74 ± .09
Autumn (Sep - Nov)		n = 12 .92 ± .05
Winter (Dec - Feb)		n = 9 .98 ± .01

TABLE 18
Ratios of Final (Evaporation-Corrected) to-Initial Concentrations of Samples Unsealed but Sheltered
from Precipitation upon Exposure for 28 Days under Field Conditions

Date Initial/Final	C_f/C_i									
	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	H ₂ ⁺	H ₄ ⁺	Cl ⁻	N-NO ₃ ⁻	SO ₄ ⁼	N-NH ₄ ⁺
830617/0719	1,1,1	1.54,1.31,1.34	1.23,1,1	2.57,1,1	1,1,1	.84,1,1	1,1,1	1,1,1	1,1,1	1,71,.66
0718/0816	.84,.92,.92	1,1,1	1,1,1	1,.63,1	1,.91,1	1,1,1	1,1,1	1.08,1.10,1.1	1,1,1	1.87,1.45,1
0812/0913	1,1,1	1.42,1.34,1.34	1,1,1	1.26,1.21,.76	.76,.81,1	1,1,1	.75,.46,.46	1.47,1.41,1.38	1,1,1	1.11,.81,.68
0908/1011	1,1	1.11,.99	1,1.3	.71,.71	1.47,1.6	1,1	.50,.50	.70,.67	1.05,1	.2,.11
1005/1108	1.08,1.08	.96,.90	1.67,1	1,1	1,1	1,1	1.27,1	1,1	1,1	.94,1.1
1103/1206	1.11,1.13,1.18	1.26,1.20,1.48	1,1,2.1	1.55,1,3.6	.48,.83,.30	.71,1,.65	1.33,1.67,2	1,1,1	1,1,1	.41,1,.95
1205/0103	1.16,1.28	1.36,1.36,1	1,1,1	*,*,*	1,.84,1	1,1,1	1,1,1	2.29,2.36,2.36	2.29,2.36,2.36	1.34,1.13,1
840103/0131	1.25,1.30,1.6	2.78,2.78,3.33	1,1,1	*,*,*	1,1,1	1,1,1	1,1,1	2.55,2.55,2.45	1,1,1	17.8,8.21
0130/0228	1.36,1.36	1,1	1.92,2.73	*,*	1,1	1,1	1,1	1,1,.85	1.47,1.42	2.97,2.42
0221/0327	1	3,4	2.09	*	1,1	1,1	1,1	1,1	1.14,1.16	1,1
0323/0424	1.16,1.52	1,2.34	1,1	*,*	1,1	1.27,1.36	1,1.12	1,1	1,1.15	.27,.31
0418/0522	1.29,1.94	2.33,3.75	1,1	*,*	1,1	1,1	1.22,1.28	1,1.05	1,1	.13,.17
0516/0619	1.89,2.11	2.08,2.15	1.8.49	1.21,3.15	1,1	1,.73	1,1	.87,.77	1,1.25	.21,1
0614/0717	.91,1.09	1,1.85	1,1	.76,1	1,1,1	1,.87,1	1,1	1,1	1,1.06	.50,.49
0713/0814	1.14,1,1	1.22,.79,1	1,1,1	1.25,.19,.54	1,1	1,1	1.36,1,1	.38,1,1	1,1,1	.71,.12,.12
0814/0911	1.07,1.09,1.12	1.08,.85,.92	13.94,1,1	2,.45,.65	0.06,1.81,1	.62,1.52,1.36	5.67,4.4.67	1,.91,1	1.20,1,1.11	.82,.05,.31
0913/1009	2,1.33,1.33	*,*,*	*,*,*	*,*,*	1,2.33,2.12	1.51,1.93,1.66	12.87,9.33,11.40	1,1,1	1.14,1.20,1	*,*,1
n:	41	42	42	42	41	41	41	42	41	42
median:	1.11	1.31	1	1.26	1	1	1	1	1	.94

* Extreme ratios not calculated because either the initial or final concentration is at the detection limit.

TABLE 19
Ratios of Final-to-Initial Concentrations of Samples Unsealed but Sheltered
from Precipitation Upon Exposure for 1 Day Under Field Conditions

Date	Vol	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	H ₂ ⁺	H ₄ ⁺	Cl	N-NO ₃ ⁻	SO ₄ ⁼	N-NH ₄ ⁺
821007	1,1,1	1,1,1	1,1,1	1.7,1,1	2.67,2,2	1,1,1	1,1,1	1.42,1.42,1.42	1,1,1	1.06,1.06,1.06	.95,1.15,1
1008	1,1,1	1.27,1,1	1,1,1	1,1,1	2,2,2	1,1,1	1,1,1	1.75,1.75,1.42	1,1,1	1.06,1,1.06	.93,.93,1
1013	1,1,1	1,1,1	1,1,1	2.08,1,1.51	1.67, 1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.93,.92,.93
1014	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.94,1.08,1
1015	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1.36,1.23
1018	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,.58	1,1,1	1,1,1	1,1,1.65
1019	1,1,1	1,1,1	1,1,1	.7,1,.7	1,1,1	1,1,1	1,1,1	.65,.65,.65	1,1,1	1,1,1	1.07,1.08,1.08
1020	1,1,1.01	1.43,1.27,1.33	1.2,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1.45,1.45,1.45	1,1,1	1.08,1.07,1.07	.95,.94,.95
1021	1,1,.99	1.46,1.46,1.42	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1.78,1.67	1,1,1	1,1,1	1,1,1
1022	1,1,1	1.19,1.19,1	1,1,1	1,.63,.80	.59,.47,.47	1,1,1	1,1.41,1	1.19,1.31,1.31	1,1,1	1,1,1	1.11,1.10,1.11
1026	1,1,1	1,1,.83	.69,.69,.69	1,1,1	.35,.35,.40	1,1,1	1,1,1	1.38,1.38,1.38	1,1,1	1,1,1	1,.96,1
1027	1,1,.99	.91,.91,.94	1.5,1.5,1.5	1,1,1	2,2,2.17	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,.97
1028	1,1,1	2.31,2.24,2.90	1.9,1.8,2.7	3.14,3.07,3.43	1.19,1.15,1.23	1,1,1	.69,.69,.55	1,1,1	1,1,1	1,1,1	1,.95,1
1029	1,1,1	.62,.60,.58	1.23,1.15,1	.59,.53,.56	.71,.57,.64	1,1,1	1,1,1	1,1,1	1.33,1.25,1.28	1,1,1	.91,.91,.93
1102	1.02,1,1	1.39,1.50,1.43	1.89,2,1.89	1.73,1.82,1.82	4,4,3.71	1,1,1	1,1,1	1,1,1	1,1.13,1.10	1,1,1	1,1,1
1103	1,1,1	1,1,1	1,1,1.19,1.24	1,1.45,1	2,2,2	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.96,.96,1
1110	1,1,0.99	1.67,1.56,2.22	1,1,1.5	1,1,1	6,6,8	1,1,1	1,1,1	.64,.57,.64	1,1,1	1,1,1	.91,.92,.91
1111	1,1,1	2,2,2.33	2,2,4	1,1,1	1,1,*	1,1,1	1,1,1	1,1,.6	1.44,1.39,1.39	1,1,1	1,1,1
840612	1,.98,1	1.52,1.19,1.23	1.33,1,1	1,1,1	1,1,1				1,1,1	1,1,1	1,1,1
0613	1,1,1	1.19,1.16,1.13	1,1,1	1,1,1	1,1,.67				1,1,1	.94,1,1	1,1,1
0614	1,1,1	1.16,1.23,1.23	1,1.22,1.22	1,1,1	1,1,1				1,1,1	1,.94,1	1,1,1
0615	1,1,1	1.23,1.19,1.23	1.22,1.22,1.22	1,1.42,1	1,1,1				1,1,1	1,1,1	1,1,1
0618	1,.97,.99	1.19,1.23,1.16	1.22,1.33,1.33	1,1,1	1,.67,.67				1,1,1	1,1,1	1,1,1
0619	1,1,1	.1,1,1	.1,1	.1,1.36,1	.51,.47	.1,1	.99,.99		.91,.91	.1,1.06,1	.1,1.05,1.05
0620	1,1,.99	1,1,1	1,1,1	.71,.64,.71	1.22,1.15,1.22	1,1,1	.99,.99,.99		.91,.91,.91	1.06,1.06,1	1.06,1.05,1.06

Table 19

Date	Vol	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	H ₂ ⁺	H ₂ ⁺	Cl ⁻	N-NO ₂ ⁻	SO ₄ ⁼	N-NH ₄ ⁺
840621	1,1,1	1,1,1	1,1,1	.64,.64,1	1,1,1	1,1,1	.99,1,.99	-	1,1,1	1,1.06,1	1.05,1.06,1.05
0622	1,.99,.99	1,1,1	1,1,1	.64,1,1	1,1,1	1,1,1	.99,1.02,.99	-	1,1,1	1,1.06,1	1.05,1.06,1.05
0623	.99,.97,1	1,1,1	1,1,1	.79,1,.79	.77,.77,.77	1,1,1	.99,1.02,.99	-	1,1,1	1,1.07,1.06	1.05,1.09,1.05
0626	1,1,1	1.14,1.12,1.1	1,.86,.86	1,1,1	.75,.55,.55	1,1,1	1,1,1.01	-	1,1,1	1,1,1	1.07,1.07,1.08
0627	1,1,1	1.12,1.14,1.1	.86,.86,.86	1,1,1	.6,.55,.55	1,1,1	1.01,1.02,1.02	-	1,1,1	1,1,1	1,1,1
0628	-1,1	-1.32,1.18	-1,1	-1.4,1	-.7,1	-1,1	-1.02,-	-	-1,1	-1,1	-1.08,1.11
0629	1,1,1	1.12,1.12,1.12	.86,.86,.86	1,1,1	.7,.7,.7	1,1,1	1.01,1.02,-	-	1,1,1	1,1,1	1.10,1.13,1.11
0630	1,.99,1	1.12,1.1,-	.86,.86,-	1,1,-	.55,.45,-	1,1,-	1.02,1.07,-	-	1,1,-	1,1,-	.87,.63,-
0704	1.01,.98,1	1,1,1	1,1,1	1,1,1	.62,.68,.62	1,1,1	1,1,1	-	-1.13,1.13	1.07,1,1	.83,.83,.83
0705	1.02,1.01,1.02	1,1,1	1,1,1	1,1,1	1,1,.68	1,1,1	1,1,1	-	1,1,1	1,1,1	.82,.83,.73
0706	1.01,-1.01	1,1,1	1,1,1	1,1,1	.68,.82,.68	1,1,1	1,1,1	-	1,1,1	1,1,1	.92,1.92
0707	-.99,.98	-1,1	-.82,.82	-1,1	-1,.55	-1,1	-1,1	-	-1,1	-1,1	-1,1
0708	.98,.98,.98	1,1,1	.82,.82,.82	3.47,1,1	.75,.62,.55	.92,1,1	1,1,1	-	1,1,1	1,1,1	.80,.88,.83
0710	.99,.97,.99	1,1,1	.88,1,.88	1,2,1	1.33,1.75,1.42	1,1,1	1,1,1	1.13,1.15,1	1.11,1,1	1.05,1.07,1.05	1,1,1
0711	-.98	-1,1	-1,-	-1,-	.1.17-	1,1,1	1,1,1	-.87,1	-1,1	-1,1	1,.83,.95
0712	-.98,1	-1,1	-1,.88	-1.67,1	-1.33,1.25	1,1,1	1,1,1	-.89,1	-1,1	-1,1	-.96,.90
0713	.99,.98,.99	1,1,1	1,1,1	1,1,1*	1.25,1,1.42	1,1,1	1,1,1	1,1,.83	1,1,1	1,1,1	.90,.89,.78
0714	.99,-1	1,-1	1,-1	1.5,-1	1,-1.25	1,1,1	1,1,1	1,-1	1,-1	1,-1	.90,-.78
0718	.99,.98,1	1,1,1	1,1,1	1,1,1	1.4,1.4,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.84,.91,.82
0719	1,.99,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0720	1,1,.99	1,1,1	1,1,1	1,1,1	1,1.2,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0721	1,1,.99	1,1,1	1,1,1	1,1,1	1,1.4,1.3	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0722	1,1,.99	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0724	1,1,1	1,1,1.13	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.66,.66,.63
0725	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,.76,.76	1,1,1	1,1,.94	.84,.81,.84

Table 19

Date	Vol	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	H _f ⁺	H _t ⁺	Cl ⁻	N-NO ₃ ⁻	SO ₄ ⁼	NH ₄ ⁺
0726	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.76,1,.76	1,1,1	1,1,1	.59,.59,.59
0727	1,1,.99	1,1,1	1,1,1	1,1,1	1,1.36,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0728	.99,1,1	1,1,1	1,1,1	2.42,1,1	2.45,1,1	1,1,1	1,1,1	1.24,1,1	1,1,1	.94,.94,.92	.63,.59,.59
0731	1,1,1	1,1,1	1.33,1.33,1.33	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0801	1,1,1	1,1,1	1.33,1.33,1.33	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.82,.79,.86
0802	1,1,1	1,1,1	1.33,1.33,1.33	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.5,.61,.79
0803	.99,.99,1	1,1,1	1.5,1.5,1.33	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.86,.79,1
0804	1,1,-	1,1,-	1.5,1.5,-	1,1,-	1,1,-	1,1,-	1,1,-	1,1,-	1,1,-	1,1,-	1,1,-
0808	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0809	-.99,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0810	1,1,1	1,1,1	1,1,1	1,1,1	.79,.79,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
0811	.99,.99,1	1.15,1.2,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.39,.39,.39	1,1,1	1,1,1	1.11,1.11,1
0813	1,1,.99	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.39,.39,.47	1,1,1	1,1,1	1.11,1,1
0814	1,1,1	1,1,1	1,1,1	1,1,1	1.96,1.96,1.79	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.89,.89,.89
0815	1,1,.99	1,1,1	1,1,1	1,1,1	1.79,1.79,1.79	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.89,.89,.89
0816	1,1,1	1,1,1	1,1,1	1,1,1	1.79,2.14,1.79	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.91,.91,.89
0817	1,1,1	1,1,.81	1,1,1	1,1	1.79,-,1.79	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.90,.91,.90
0818	1,1,1	1,1,1	1.25,1.25,1.25	1,1,1	1.96,1.81,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	.91,.91,.91
0822	1.99,1	1.13,1,1	1.32,1.32,1.32	1,1,1	1.96,1,1	1,1,1	1.02,1,1	2.8,2.8,2.8	.86,.89,.89	1,1,1	1,1,1
0823	1,1,1	1.13,1.13,1	1.32,1,1	1,1,1	1,1.96,1	1,1,1	1,1.03,1	3.2,2.6,2.6	1,1,.89	1,1,1	1,1,1
0824	1,1,1	1,1.13,1	1,1,1	1,1,1	1,1,1	1,1,1	.97,1,1	2.6,2.6,2.6	1,1,1	1,1,1	1,1,1
0825	1,1,1	1,1.13,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	2.4,2.8,2.8	1,1,1	1,1,1	1,1,1
0826	1,1,1	1.13,1,1	1.45,1,1	1,1,1	3.04,1,3.48	1,1,1	1,.97,.97	2.6,2.8,3.6	1,1,1	1,1,1	1,1,1.03
0830	1,1,1	1,1,1	1.23,1.30,1.30	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1.09,1.09,1.07
0831	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1.07,1.07,1.07
n	216	217	216	216	214	205	205	162	217	217	218
Median	1	1	1	1	1	1	1	1	1	1	1

TABLE 20
Bartlett Linear Regression of Sangamo Cumulative (Y)
vs. Aerochem Metrics Accumulated Daily (X) Results

Parameter	n	Concentration			Deposition			Loading		
		r	S	I	r	S	I	r	S	I
H_t^+	55	0.87	0.97*	0.01*	0.94	1.01*	-0.06*	0.95	0.86	0.38
H_f^+	55	0.88	1.00*	0.01*	0.97	1.18	-0.30	0.96	0.99*	0.09*
$SO_4^{=}$	55	0.92	1.20	0.02*	0.97	1.15	0.70*	0.98	0.94	18.48
$N-NO_3^-$	56	0.89	1.08*	0.03*	0.94	1.05*	1.32*	0.95	0.91	3.27
Ca^{++}	56	0.82	1.44	-0.01*	0.87	1.37	-0.92*	0.88	1.18	0.35*
Cl^-	50	0.69	0.86	0.01*	0.76	0.80	0.68*	0.81	0.81	0.27*
Mg^{++}	54	0.68	1.55	-0.01*	0.69	1.52	-0.45*	0.59	1.42	-0.25*
K^+	49	0.53	0.57	0.01	0.57	0.70	0.54	0.55	0.72	0.30*
Na^+	54	0.56	0.78	0.01*	0.71	0.65	0.72*	0.71	0.64	0.57
$N-NH_4^+$	52	0.79	1.21	0.01*	0.86	1.22	-0.45*	0.89	1.00*	2.48
SDP**	58	0.92	0.94*	0.01*						
GDP**	58	0.98	0.96	0.01*						

* Slope (S) no different from unity and intercept (I) no different from zero at the 95% confidence level.

** SDP = sample depth and GDP = gauge depth

TABLE 21
Bartlett Linear Regression Results of Evaporation Corrected Data
Cumulative (Y) vs. Accumulative Daily (X)

Parameter	n	Concentration			Deposition		
		r	S	I	r	S	I
H_t^+	55	0.83	0.78	0.00*	0.95	0.83	-0.15*
H_f^+	55	0.86	0.78	0.01*	0.96	0.97*	-0.28
$SO_4^{=}$	55	0.92	1.01*	-0.08*	0.98	0.94	-2.20*
$N-NO_3^-$	56	0.82	0.87	0.02*	0.95	0.89	-0.05*
Ca^{++}	56	0.85	1.12	-0.00*	0.92	1.11	-1.03
Cl^-	50	0.68	0.69	0.01*	0.77	0.73	-0.15*
Mg^{++}	54	0.63	1.30	-0.01*	0.62	1.28	-0.44*
K^+	49	0.65	0.54	0.01*	0.68	0.59	0.33
Na^+	54	0.49	0.58	0.01*	0.73	0.56	0.41
$N-NH_4^+$	52	0.76	0.93*	0.02*	0.89	0.97*	-0.44*

* Slope (S) no different from unity and intercept (I) no different from zero at the 95% confidence level.

TABLE 22
Comparison of Cumulative Sangamo vs. Aerochem Metrics Accumulated Daily Data*

Parameter	n	Concentration			Loading			Deposition		
		D	B	BP	D	B	BP	D	B	BP
H _t ⁺	55	6.62	0.00	1.30	8.43	-0.30	-2.04	7.73	0.00	-1.04
H _f ⁺	55	11.96	0.01	3.50	10.11	0.07	-0.40	9.67	0.38	0.85
SO ₄ ⁼	55	9.24	0.43	9.26	7.68	8.50	6.05	7.46	27.53	7.00
N-NO ₃ ⁻	56	6.67	0.06	6.83	6.08	1.09	3.44	6.90	2.77	4.24
Ca ⁺⁺	55	20.04	0.06	11.73	18.86	2.32	9.62	20.38	3.63	9.15
Cl ⁻	50	10.72	-0.01	-5.34	13.08	-1.12	-9.12	14.25	-1.08	-7.76
Mg ⁺⁺	54	16.49	0.01	4.36	18.99	0.51	0.97	20.35	0.67	1.95
K ⁺	49	22.06	-0.00	-6.12	21.81	-0.34	-10.10	22.93	-0.29	-8.85
Na ⁺	54	20.03	-0.00	-6.14	21.84	-0.49	-9.16	17.03	-0.54	-8.08
N-NH ₄ ⁺	52	8.79	0.07	7.57	7.73	2.42	3.18	9.02	4.66	4.87
Eff. **	58	6.43	-2.36	-1.24	-	-	-	-	-	-
SDP **	58	6.22	-3.88	-3.40	-	-	-	-	-	-
GDP **	58	2.80	-3.14	-2.16	-	-	-	-	-	-

* D = median absolute percentage difference; B = Bias and BP = normalized percentage bias (see Section 3.1 for formulations);

** Eff. = collection efficiency; SDP = sample depth and GDP = gauge depth.

TABLE 23
Summary of Sangamo Cumulative (c) and Aerochem Metrics Accumulated
Daily (d) Precipitation Depth Comparison

Site	Collection Date (of a 28 d sample)	McRc= $\frac{\text{Sample Depth (c)}}{\text{Sample Depth (d)}}$	D= $\frac{\text{Gauge Depth (c)}}{\text{Gauge Depth (d)}}$
Dorset	800731	0.86	1.00
	0902	0.84	1.10
	0930	0.65	0.94
	1231	0.74	0.96
	810130	0.71	1.13
	0227	0.67	0.84
	0331	0.69	0.96
	0430	0.77	1.02
	0529	0.72	1.12
	0630	0.77	1.03
	0731	0.82	0.98
	0831	0.94	0.87
	0930	0.83	1.24
	1030	0.77	1.05
	1130	0.22 *	1.01
	820105	0.62	0.92
	0202	0.58	0.75
	0302	0.75	0.96
	0330	0.74	0.84
	0427	0.92	1.09
	0525	0.66	0.93
	0622	0.89	0.96
	0720	0.83	0.96
	0817	0.82	0.76
	0914	0.81	0.89
	1012	0.90	1.08
	1109	0.86	0.87
	1207	0.88	0.99
	830104	0.75	0.91
	0201	0.74	0.91
	0301	0.81	0.86
	0329	0.70	0.94
	0426	0.80	0.95
	0524	0.86	0.96
	0621	0.66	0.78
	0719	0.92	0.98
	0816	0.88	0.87
	1011	0.90	0.96
	1108	0.87	0.92
	1206	0.78	0.90
	840103	0.65	0.76

TABLE 23 (Cont'd)
Summary of Sangamo Cumulative (c) and Aerochem Metrics Accumulated
Daily (d) Precipitation Depth Comparison

Site	Period	McRc= $\frac{\text{Sample Depth (c)}}{\text{Sample Depth (d)}}$	D= $\frac{\text{Gauge Depth (c)}}{\text{Gauge Depth (d)}}$
Fernberg	820505	0.45*	1.00
	0622	0.59	1.00
	0720	1.12	1.00
	0817	0.76	0.89
	0914	0.61	1.00
	1012	0.85	1.00
	830201	0.74	1.00
	0329	0.92	1.00
	0426	0.44*	1.00
	0621	0.60	0.69
	0719	0.69	1.00
	0816	0.83	1.00
	0913	0.96	1.00
	1011	0.86	0.86
	1206	0.56	1.05

All:	0.78 ± 0.11 (n=53)	0.95 ± 0.10 (n=56)
Summer:	0.81 ± 0.12 (n=32)	0.96 ± 0.11 (n=32)
Winter:	0.74 ± 0.10 (n=21)	0.95 ± 0.09 (n=24)

* Not used in the calculation.

TABLE 24
Summary of Sangamo Cumulative (c) vs.
Aerochem Metrics Accumulated Daily (d) Data for Acid/Base Ions

Parameter	n	$M_c = \frac{\text{Loading(c)}}{\text{Deposition(d)}}$	$R_c = \frac{\text{Concentration(d)}}{\text{Concentration(c)}}$	$\frac{\text{Deposition(c)}}{\text{Deposition(d)}}$
H_f^+	51	0.86 ± 0.25	0.94 ± 0.26	1.07 ± 0.27
H_t^+	53	0.82 ± 0.26	0.97 ± 0.25	1.08 ± 0.54
$SO_4^{=}$	54	0.93 ± 0.23	0.85 ± 0.16	1.17 ± 0.26
$N-NO_3^-$	55	0.87 ± 0.21	0.89 ± 0.16	1.10 ± 0.22
$N-NH_4^+$	50	0.92 ± 0.28	0.88 ± 0.32	1.17 ± 0.35
Overall * Average		0.88	0.91	1.12

TABLE 25

**Bartlett Linear Regression of Metrex AS-2 Cumulative (X)
vs. Metrex SAS 8-25 Daily (Y) Sampling Air Concentration Results**

Parameter	n	r	S	I
SO ₂	18	0.82	0.90*	1.21
SO ₄	17	0.87	1.02*	-0.22*
Total N-NO ₃ ⁻ +	17	0.94	0.83	0.04

* Slope (S) no different from unity and intercept (I) no different from zero at the 95% confidence level

+ total N-NO₃⁻ = N-NO₃⁻(p) + N-HNO₃(v)

TABLE 26

Comparison of Cumulative Metrex AS-2 vs. Daily SAS 8-25
Air Concentration Results*

Parameter	n	D	B	BP
SO ₂	18	12.98	-0.83	-10.7
SO ₄	17	4.21	0.15	3.37
Total N-NO ₃ ⁻ +	17	3.10	0.03	4.22

* D = Median absolute difference; B= Bias and BP = normalized bias
(see section 3.1 for formulation)

+ total N-NO₃⁻ = N-NO₃⁻(p) + N-HNO₃(v)

WHC/en
ASP2/22b